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TEMPO radicals as EPR probes to monitor the adsorption of different species into X zeolite

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Abstract

A computer-aided analysis of the electron paramagnetic resonance (EPR) spectra of TEMPO radicals adsorbed in X zeolites is performed under various experimental conditions, both in the absence and in the presence of various species. In dehydrated NaX zeolites the radical gives rise to two superimposed signals corresponding to species characterized by different mobility and polarity and by a different temperature dependence. Controlled addition of water leads to an increase of mobility up to 4.2 water molecules per supercage. Under conditions of partial hydration, the radicals show an increase in the correlation time for motion with an increase in the size of the cation in the exchanged zeolites, whereas an increase in mobility is found upon going from NaX to NaY samples. These results are analyzed in terms of the variation of the local electric field at the surface. Dipolar broadening is shown to be responsible for the line shape variations found at TEMPO loadings up to 0.32 molecules per supercage. Heisenberg spin-spin interactions also become relevant at higher loading. Increasing amounts of 2,2,6,6-tetramethylpiperidine induce a restriction of mobility. This result is interpreted in terms of a decrease in the free volume available to radicals which occupy the zeolite cavities. However, loading of pentane leads to a similar increase in mobility as found with increasing amounts of water. The environmental polarity, as expected, decreases due to the replacement of water molecules with pentane. It is proposed that the zeolite hosts, when saturated with pentane, slow moving radicals which are trapped in the pores.

Keywords: Adsorption; electron paramagnetic resonance spectra; TEMPO radicals; X zeolite.

Introduction

The faujasite cavities of the NaX zeolites can comfortably host guest molecules with diameters up to 0.7-0.75 nm, since the kinetic diameter of the cavity window is about 0.8 nm [1]. On the contrary, only small species may enter the sodalite cavities (diameter, 0.22 nm).

Both the hydrated and dehydrated zeolites are known to present a locally homogeneous distribution of cations and surface groups (both O⁻ and OH) [2]. Furthermore, the faujasite cavities bear different adsorption sites, termed Sites II and III

[3]. Paramagnetic probes may localize in sites characterized by different environmental mobility and polarity at the zeolite surface. In this case, the electron paramagnetic resonance (EPR) technique can give very precise structural and dynamical information about the probes and their environments by means of an accurate analysis of the spectral line shape [4]. Under conditions where the exchange rate among different sites is slow on the EPR time scale, i.e. less than $(2-3) \cdot 10^7$ s⁻¹, the corresponding EPR signals at each site contribute as superimposed absorptions to the overall spectra. Due to their ability to interact with the surface sites, and due to the excellent methods for detailed analyses of the spectral line shape, both paramagnetic metal ions [5-11] and nitroxide radicals

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[4,12-17] behave as good spin probes in zeolites X and Y.

In the present work we have chosen the 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) radical as EPR probe to obtain information on the interactions of guest species with the zeolite surface under different experimental conditions. The diameter of the smallest cylinder (critical diameter) of the radical, that is about 0.65 nm, permits access to the faujasite cavities [18,19]. The selected species, including the probe itself, present different sizes, polarities and abilities to interact with the zeolite surface. The computer-aided spectral analysis, by means of suitable programs, allowed us to evaluate both the magnetic parameters, i.e. the g and nitrogen hyperfine tensor components, and the parameter for motion, i.e. the correlation time for motion τ . The parameters were measured as a function of the extent of hydration, the loading of probe, the temperature, and the presence of different guest molecules.

Experimental

The TEMPO radical employed in this investigation was obtained from Aldrich and was used as received. The samples of the zeolites LiX, NaX, and KX (Si/Al, 1.22), and the zeolite NaY (Si/Al, 2.36) were generous gifts from Dr. E. Flanigen of Union Carbide Tarrytown Technical Center. Zeolite samples for EPR measurements (about 40 mg) were calcined individually in the open air for 12 h at 550°C and allowed to cool down to room temperature in a desiccator before exposure to pentane solutions of TEMPO. The adsorption of TEMPO from pentane solutions at various concentrations was controlled spectrophotometrically at 220 nm. To eliminate both residual pentane and oxygen, all samples were evacuated to 0.1 Torr and sealed in Pyrex containers (internal diameter about 2 mm). The adsorption isotherm of TEMPO in NaX from pentane solutions reveals an efficient uptake up to a saturation value of about 3.54 mol g⁻¹ (5.6 wt%). These samples were employed for the study of the effects of loading and spin-spin

interactions. Furthermore, the EPR spectra of the dry NaX sample (containing 0.011 TEMPO molecules per supercage) were recorded at various temperatures. Another set of related samples was prepared with a constant amount of 0.011 TEMPO molecules per supercage and different amounts of 2,2,6,6-tetramethylpiperidine (a diamagnetic guest molecule which mimics TEMPO in size and shape). The water content was controlled gravimetrically before the EPR measurements. The samples used for variable hydration experiments were prepared using water vapor transferred from a water reservoir with a gentle stream of argon gas. The extent of hydration was determined gravimetrically. An additional set of dry samples was exposed to pentane vapor which was carried into the sample in a stream of argon.

The EPR measurements were repeated for various samples, under the same experimental conditions, by also using zeolites from different preparations. Therefore, the reliability of the results could be assessed from their reproducibility.

All EPR measurements were performed on a Bruker ESP300 interfaced to a computer with the ESP1600 software system. Temperature control was achieved with a Bruker ER 4111T temperature controller ($T = 20 \pm 1^\circ\text{C}$).

The accuracy of the parameters evaluated from computation of the EPR spectra is as follows: $\tau = \pm 0.05 \cdot 10^{-9}$ s; $A_{ii} = \pm 0.05$ G; $g_{ii} = \pm 0.00005$.

Results and discussion

TEMPO radicals in dehydrated NaX zeolites

To obtain information on localization and mobility of the probe in the faujasite cavities, the radicals adsorbed in dehydrated zeolites were studied at different temperatures. Figure 1 shows the EPR spectra of 0.011 TEMPO molecules per supercage adsorbed in dehydrated zeolites at three representative temperatures: 273, 293 and 313 K. The radicals at room, and lower, temperature give rise to an almost rigid signal, which corresponds to $\tau > 5 \cdot 10^{-7}$ s for typical nitroxide radicals, but

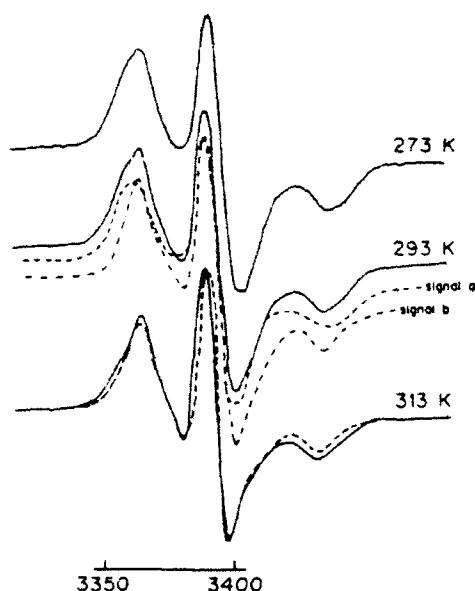


Fig. 1. Experimental (full lines) and computed (dashed and dotted-dashed lines) EPR spectra of 0.011 TEMPO molecules per supercage adsorbed into dehydrated NaX zeolite at different temperatures.

the line shape analysis indicated that the mobility increases with the increase in temperature. Even the room temperature signal was rather broad, probably due to small spin-spin effects. In spite of this, two contributions were recognizable which arose from radicals in two different environments, characterized by different mobility and polarity. Indeed the line shape at 293 K was fitted by adding the two computed signals (at 1:1 ratio) shown as dashed and dashed-dotted lines below the spectrum (signals a and b respectively). Signal a was obtained as a rigid powder spectrum by using the program Sim15fi which assumes a random orientation of spins and performs a double numerical integration over an octant of the unit sphere. Non-axial *g* and hyperfine tensors were considered in the simplified Hamiltonian: $H = \beta(g_{zz}S_zH_z + g_{xx}S_xH_x + g_{yy}S_yH_y) + (A_{zz}S_zI_z + A_{xx}S_xI_x + A_{yy}S_yI_y)$ (*g* tensor components, 2.0097, 2.0064 and 2.0025; A_N tensor components, 7.0, 8.0 and 37.5 G).

The relatively high values of the mean hyperfine coupling ($\langle a \rangle = (1/3)(A_x + A_y + A_z)$), determined from the fitting program, indicated high polariza-

tion of the spin density in the N-O group, due to the significant surface electric field, together with the formation of an electric quadrupole moment [13,14]. Signal b was computed by using the program written by Schneider and Freed [20] for slow-moving nitroxide radicals ($5 \cdot 10^{-7}$ s $> \tau > (2-3) \cdot 10^{-9}$ s) which also includes linewidth calculation from relaxation parameters. Brownian diffusion was assumed to modulate the magnetic tensor components, with $\tau = 2 \cdot 10^{-8}$ s. The intrinsic linewidth used for computation was 3.5 G, which indicated a small contribution from dipolar broadening. This relatively narrow linewidth also demonstrated that the evacuation procedure used to prepare these samples was effective in removing almost all the oxygen from the cavity network. Indeed, we found that unevacuated samples show a large dipolar broadening of lines. The *g* tensor components were the same as for signal a, whereas a decrease of the A_N components was implemented to improve the fitting ($A_{xx} = 5.5$ G, $A_{yy} = 7.5$ G, $A_{zz} = 36.5$). The low rotational mobility of the radicals should exclude the possibility that non-interacting species are moving freely in the zeolite supercages. However, the permanent dipole moments of the nitroxides also guarantee their interaction with the electrostatic field of the ionic zeolite structure. The low mobility of the species prevented any attempts to calculate the exchange rates between the different moving radicals by means of the method proposed by Davoust and Devaux [21]. We propose that the two contributions arise from radicals sitting in separate cavities at Sites III (on the surface of the large cavities) and II (in the large cavities close to the sodalite cage) respectively, as already found for ClO₂ molecules [22]. Both types of sites provide ready interactions with polar molecules. Indeed the 48 Sites III in the dehydrated NaX contain only four Na⁺; this corresponds to a much smaller interaction probability with respect to the 32 Na⁺ at the 32 Sites II [1]. The electric field is stronger at Sites III than at Sites II and the cations at Sites III are poorly shielded [23]. Therefore, the radicals should preferentially interact at Sites III where the N-O

groups experience a rather strong spin polarization. These findings account well for the lower mobility (as sensed by the correlation time for motion) and the higher environmental polarity (as sensed by the hyperfine coupling tensor) of the radicals which are supposed to interact at Sites III. Similar conclusions have been drawn by EPR studies on fully solvated X zeolites containing nitroxide radicals, even when the solvation strongly modified the mobility of the radicals [14].

However, other effects can also be proposed to explain the results.

(1) The persistence in some sites of water molecules may lead to the increase of mobility (see below). Nevertheless, this possibility is unlikely because (a) the samples were thoroughly dehydrated; (b) results from different preparations were reproducible under the same experimental conditions and (c) higher A_N tensor components were found in the presence of added water molecules (see below). Therefore we conclude that the presence of signal b cannot be ascribed to water molecules surrounding the radicals.

(2) The localization of some of the radicals may be on the external surface of the zeolites. Of course the preparation procedure cannot prevent some radicals from being localized on the external surface. Indeed, in such a case, the external and internal sites should show different radical mobilities upon addition of water. However, since only one component was present in the hydrated samples (see below), it is reasonable to suppose that the largest part of the radicals is adsorbed into the cavities.

(3) The presence of impurities may create a different environment for the radicals. The reproducibility of the results with zeolites from different preparations (and purifications) seems also to exclude this last possibility.

The increase of temperature (spectrum at 313 K in Fig. 1) produced an increase of mobility of the two signals. The dashed line, which is superimposed on the 313 K spectrum, was obtained with the same magnetic parameters and line width as signal b at 293 K, but $\tau = 8.5 \cdot 10^{-9}$ s. The line shape

corresponding to signal a was no more clearly defined and an arbitrary fitting could be obtained by decreasing line width or hyperfine coupling, or by increasing mobility. However, the spectrum at lower temperature (273 K in Fig. 1) showed almost a collapse of the two signals due to restriction of mobility of signal b. Therefore both signals a and b showed temperature dependence, although signal a presented a lower variation of the correlation time for motion with temperature, as compared to signal b. The low accuracy in the determination of the motion parameters did not allow for a quantitative evaluation of the activation energy for motion. However, the activation energy for rotational motion was clearly lower for signal a than for signal b. A decrease of the activation energy with respect to unadsorbed nitroxide solution is typical of radicals interacting at surface sites in restricted space [14].

Effect of water addition into dehydrated TEMPO-containing NaX zeolites

Figure 2(a) shows the effect produced by a controlled addition of water on the lineshape of dehydrated NaX zeolite containing 0.011 TEMPO molecules per supercage. Only one spectral component was identifiable in the experimental spectra reported in Fig. 2(a). A further consequence of the water addition was a progressive increase of mobility. Indeed, the spectrum at 4.2 water molecules per supercage (4.6 wt% corresponding to 2.5 mmol g⁻¹) was computed (dashed line) as a single line signal with $\tau = 7.5 \cdot 10^{-9}$ s (A_N tensor components, 6.5, 8.0 and 36.9 G), whereas from 12 to 26.3 molecules per supercage the correlation time for motion underwent only a small change from $4.5 \cdot 10^{-9}$ to $4.0 \cdot 10^{-9}$ s.

It was apparent that a very small amount of water (about four water molecules per supercage) was enough to change both the localization (at Site II) and the mobility (τ increased from $2.0 \cdot 10^{-9}$ to $7.5 \cdot 10^{-9}$ s) of the radicals. It is well known that water molecules are hosted in both the sodalite and faujasite cavities and about 24 water molecules

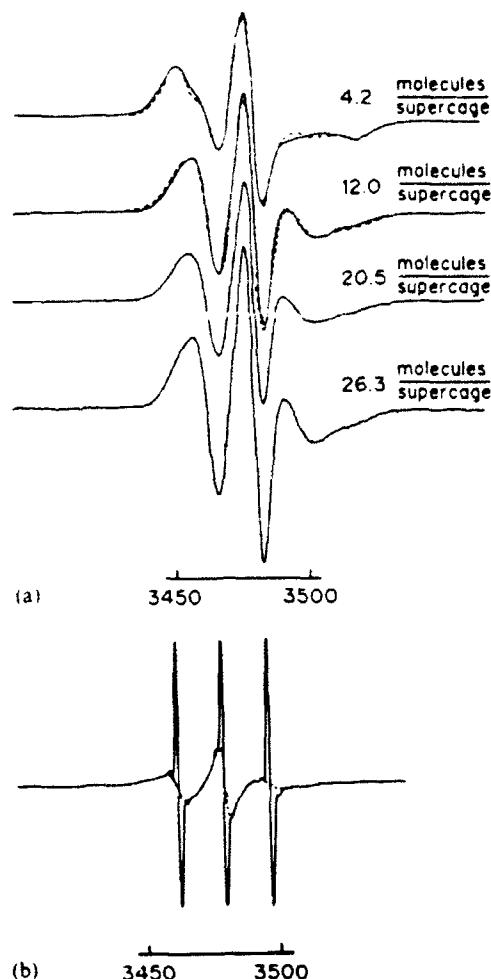


Fig. 2. (a) Experimental (full lines) and computed (dashed lines) EPR spectra of 0.011 TEMPO molecules per supercage adsorbed into NaX zeolite at different water uptakes (indicated in molecules per supercage). (b) Experimental (full line) EPR spectrum of 0.011 TEMPO molecules per supercage adsorbed into wet NaX zeolite. The dashed line was obtained by subtraction of the "free radicals" component (see text).

per supercage represents the hydration layer of Na cations at the surface [1]. The dehydration curve of this 24 molecules per supercage structure presents a continuous pattern, thus indicating the same physicochemical properties for all water molecules. Since the radical molecules can only enter the faujasite cavities, they may localize in sites, like Sites II, in which the cation-water enrichment ensures also hydration of the radical with consequent lack of interaction with the surface and

increase of mobility. Therefore, it was assumed that the preferential hydration of the cations at Sites II forced the radicals to move to such sites, and the two-site distribution characterizing the dehydrated zeolite (corresponding to signals a and b) was completely lost. However, the almost constant "slow" mobility, which was found for the radicals at hydration ≥ 10 molecules per supercage, indicated that a further hydration of the radicals was prevented. Since only four of the eight Na^+ cations per supercage are considered as active sites in the large zeolite voids [1], the mobility of each radical hosted in a large void increased up to 2-3 water molecules per cation ("saturation" conditions). Further hydration did not modify the radical mobility, probably due to preferential interaction of these partially hydrated radicals with the zeolite surface. This is in very good agreement with previous results by nuclear modulation in the spin echo patterns [17]. These results indicate that only four deuterium nuclei, belonging to two or three D_2O molecules, are in close proximity to the N-O group, even in fully hydrated NaX zeolites. However, our results also correlate well with the results from the calorimetric measurements reported in Ref. [24]. The authors have found that the calorimetric pattern as a function of water uptake gave a plateau at uptakes $\geq 4-6$ water molecules per supercage. This has been interpreted in terms of a limited cation hydration at the zeolite surface.

The signal showing $\tau \approx 4 \cdot 10^{-9}$ s was still present in wet samples, superimposed on the three-line, fast-motion signal (Fig. 2(b)). The dashed line was obtained by subtraction of the fast-motion component. Therefore a fraction of the radical (about 40%) remained at the zeolite surface, whereas another fraction gave rise to a contribution in fast-motion conditions ($\tau \approx 1 \cdot 10^{-11}$ s) due to radicals in "pockets" of water and not interacting with the zeolite surface.

NMR analysis to characterize the status of zeolitic water [25-28] has indicated rapid exchange (on the NMR time scale) of water molecules among different sites, even if localized in different cavities.

The different time scale of EPR allows the identification of different environments for the radical probe, which correspond to water molecules bound to different sites, or characterized by different viscosity as a function of the distance from the surface. Indeed, a gradient of viscosity has been found for fully hydrated zeolites, from the surface to the pore bulk [12-14].

Effect of cation exchange in X zeolite and comparison between NaX and NaY zeolites

In Fig. 3 the spectrum of TEMPO radicals (0.011 molecules per supercage) in NaX zeolite, hydrated at 22-25 water molecules per supercage, is compared with the signals obtained with LiX and KX zeolites and with NaY zeolite at the same water and radical contents. In all cases the dashed lines reproduce the spectra computed by means of the Schneider-Freed program [20]. We selected these three alkaline cations since they are characterized

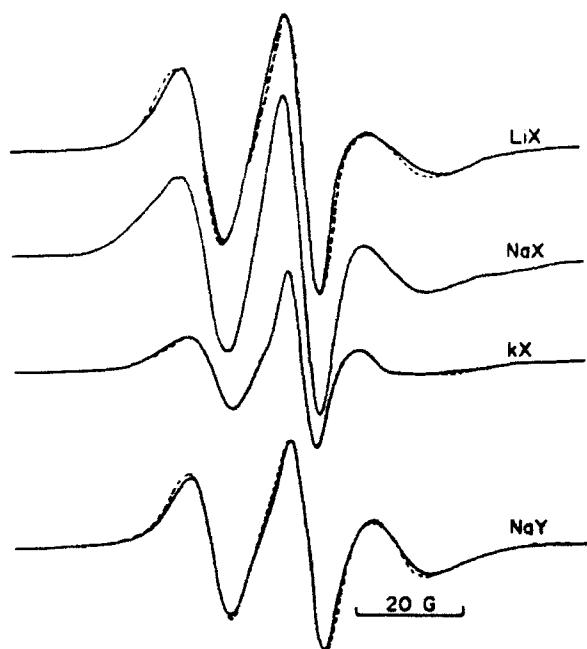


Fig. 3. Experimental (full lines) and computed (dashed lines) EPR spectra of 0.011 TEMPO molecules per supercage adsorbed into LiX, NaX, KX, and NaY zeolites, hydrated at 22-25 molecules per supercage.

by similar physicochemical behavior, the same charge, but a different charge/size ratio. Therefore, attention was focused on the influence of this last parameter on the surface potential, which in turn affects the radical-surface interaction. Furthermore, hydrated samples were preferred to the dehydrated ones, since the two-site distribution complicated the spectral analysis more. The line shape analysis for the series LiX-NaX-KX indicated an increase of the correlation time for motion with the increase of the cation size. With respect to the TEMPO-NaX system for which $\tau = 4.0 \cdot 10^{-9}$ s, LiX and KX spectra were computed by using in the calculation $\tau = 3.0 \cdot 10^{-9}$ s and $\tau = 4.7 \cdot 10^{-9}$ s, respectively. However, for KX a tilt of the main rotational axis of 80° was also considered to improve the fitting, which was a further indication of a stronger interaction of the radical with surface sites, with a change of the main rotational axis along the N-O direction. This result might be analyzed in terms of the variation of the local electric field; the adsorbate interaction with the surface was stronger since the larger cations moderately competed with the radicals for interacting at the surface sites. However, it has been found [1] that K ions are less hydrated than Na ions at Sites II in zeolite. Therefore, even if the total level of hydration was almost the same, a lower hydration at Sites II might be also responsible for the increase of correlation time for motion. In Fig. 3 the spectrum of a TEMPO-NaY sample is also shown. In this case, the variation of the local electric field at the surface and the corresponding decrease of cation density and hydration state well explained the increase in mobility in going from NaX to NaY samples. Indeed, in this last case the spectrum was computed with $\tau = 2.5 \cdot 10^{-9}$ s. Previous studies on the adsorption of positively charged cations in X and Y zeolites [12,29] have shown that positively charged species have a larger affinity for the lattice of Y zeolites than X zeolites. Our finding of a stronger interaction of the neutral TEMPO with the X zeolite supported the explanation given by the above authors. They invoked a charge effect together with different hydration states to explain

the stronger interaction with the surface in Y zeolites.

Effect of increasing TEMPO loading in NaX zeolite

In order to investigate how the TEMPO radicals distribute in the network of the zeolite supercages, by interacting with surface sites, NaX samples were analyzed at various TEMPO loadings. Figure 4 shows the variation in EPR line shape with the increase in the molecules of TEMPO per NaX supercage (hydrated at about 15 water molecules per supercage). The dashed lines are the spectra computed with the aid of the Schneider-Freed program [20], by using, in all cases, the same magnetic and mobility parameters as used in the

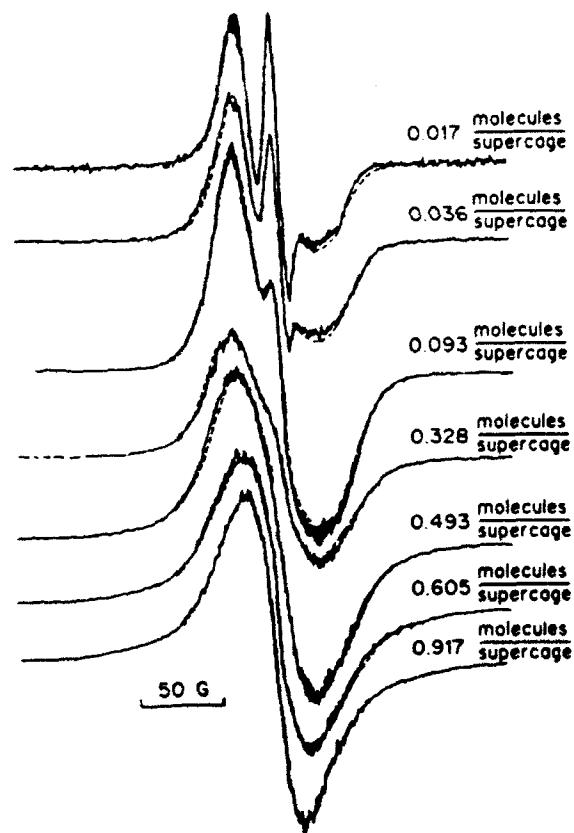
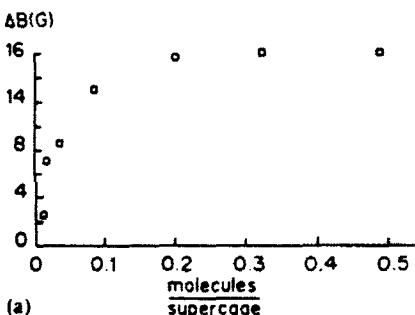


Fig. 4. Experimental (full lines) and computed (dashed lines) EPR spectra of NaX zeolites (hydrated at about 15 water molecules per supercage) at different TEMPO loadings, indicated as TEMPO molecules per supercage.

computation of the spectrum in Fig. 2 for 0.011 TEMPO molecules per supercage and 12 water molecules per supercage. For instance, the correlation time used for computation was $4.5 \cdot 10^{-9}$ s. The linewidth was the only parameter which was changed by the increase in loading up to ≈ 0.33 molecules per supercage. Figure 5 reports the variation of linewidth as a function of the radical content. Slowly moving radicals usually undergo such a line broadening because of dipolar-dipolar interactions, due to radicals hosted in nearby cavities. However, at TEMPO concentrations larger than 0.3 molecules per supercage, the spectra also showed line narrowing typical of Heisenberg exchange interaction. For instance the spectrum at 0.33 molecules per supercage was computed by using an intrinsic linewidth of 16 G and exchange



(a)

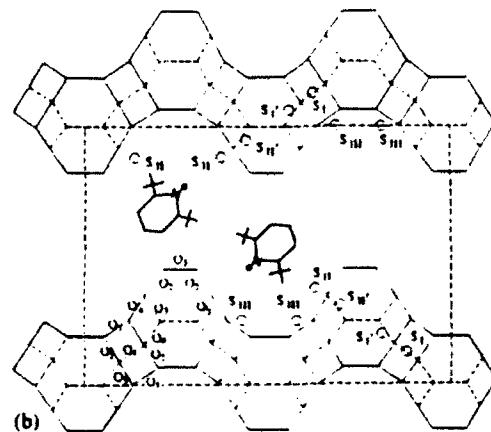


Fig. 5. (a) Variation of the linewidth (ΔB) used for the computation of the spectra, as a function of TEMPO molecules per supercage. (b) Schematic picture of a possible molecular arrangement for Heisenberg exchange interaction between two TEMPO molecules.

frequency $\omega \approx 2.5 \cdot 10^7 \text{ s}^{-1}$. However, the fitting of the spectra at 0.5 and 0.6 molecules per supercage was obtained by using a constant linewidth of 16 G (in any case, an increase in linewidth of 1 G only slightly affected the line shape and the linewidth of the computed spectra), whereas the exchange frequency was increased up to $4 \cdot 10^7$ and $8 \cdot 10^7 \text{ s}^{-1}$ respectively. This behavior is expected for increasing TEMPO concentration due to localization in proximate sites at the zeolite surface. The steric hindrance for two TEMPO molecules present in the same supercage is very high. Nevertheless, we suppose that two N-O groups have good probability of facing each other in two proximate cavities at high loading, giving rise to Heisenberg spin-spin interactions (a schematic picture of a possible molecular arrangement is shown in Fig. 5).

Our results are comparable to some extent with previous results obtained for water solutions of nitroxide radicals adsorbed into homoporous silica gels [30-32]. First of all the authors have found restriction of mobility for the radicals hosted in narrow pores [30,31]. Then, dipole-dipole broadening prevails with the increase of probe concentration [32]. The evaluation of the mean distance d between radicals may be performed by means of the contribution to the linewidth due to dipole-dipole interaction [33]

$$\Delta B_D = 3 \cdot 10^{-20} / d^3$$

The dipole-dipole contribution to the linewidth ΔB_D was roughly evaluated by subtracting the linewidth obtained at low loading, i.e. conditions under which the linewidth was invariant to small changes of TEMPO concentration. On this basis, for instance, the main distance at 0.036 molecules per supercage was found to be about 1.6 nm, whereas at 0.33 molecules per supercage the calculation gave 1.0 nm.

To test the reasonableness of our hypothesis that, at high loading, the radicals localize in proximate cavities, and, two-by-two, may occupy the same cavities, we performed a statistical simulation of the distribution of TEMPO molecules in the zeolite cavities. A two-dimensional square lattice

was used to represent the diamond connectivity of the X zeolite; we also assumed that a supercage may be occupied by either one or two TEMPO molecules. The occupancy of the zeolite cavities was described using x as the number of TEMPO molecules per supercage. The following equations were derived from the model:

(a) for p_1 , the probability that one TEMPO occupies one supercage

$$p_1 = x \cdot 2(1 - x)2^4$$

(b) for p_2 : the probability that two TEMPO molecules are in the same supercage

$$p_2 = x^2 \cdot 4$$

(c) for p_{s1} , the probability that one or two TEMPO molecules occupy isolated cavities.

$$p_{s1} = (p_1 + p_2)[1 - (p_1 + p_2)]^4 = pq^4$$

where $p = p_1 + p_2$ and $q = 1 - p$

(d) for p_{s2} , p_{s3} , p_{s4} , and p_{s5} , the probabilities that one or two TEMPO molecules occupy two, three, four, or five proximate cavities

$$p_{s2} = p^2 q^6; p_{s3} = p^3 (q^7 + q^8);$$

$$p_{s4} = p^4 (3q^8 + q^9 + q^{10});$$

$$p_{s5} = p^5 (q^8 + q^9 + 3q^{10} + q^{11} + q^{12})$$

Since the maximum loading was rather low, clusters of up to five adjacent cavities were enough to account for almost all the probabilities.

In Fig. 6 the total averaged probabilities that TEMPO molecules occupy isolated cavities or two, three, four, and five close cavities, indicated as $Y_i = p_{s_i} / \sum p_{s_i}$, are reported as a function of the occupancy. These data indicated that increasing the loading of TEMPO led to about 20% probability that two proximate cavities are occupied by one TEMPO molecule each. The plateau was reached (saturation condition) at $x = 0.8-1.0$ molecules per supercage. Of course the probability was lower for a larger number of occupied neighboring cavities. By taking into consideration all the different radical clusters, and in the limits of the low accuracy

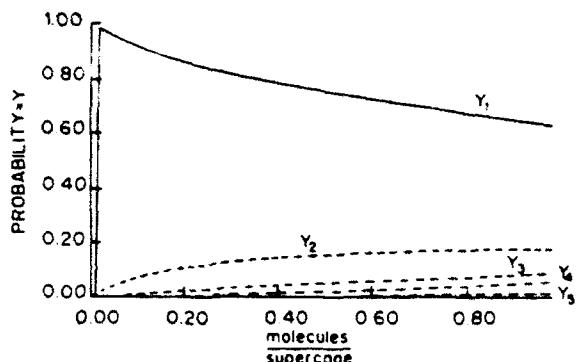
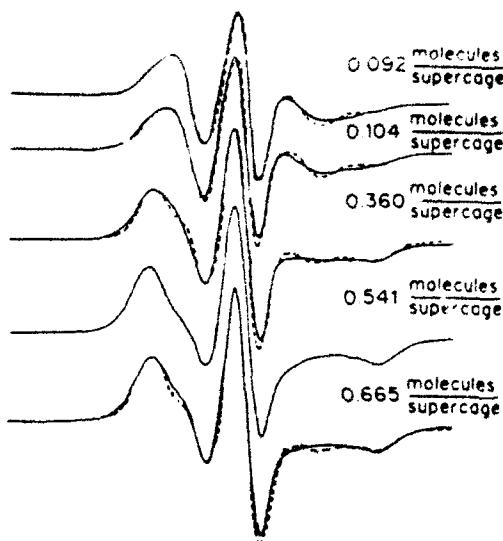


Fig. 6. Relative averaged probabilities that TEMPO molecules occupy isolated cavities or two, three, four, and five close cavities (these probabilities are indicated as y_1 , y_2 , y_3 , y_4 , and y_5 , respectively) as a function of the occupancy (molecules per supercage).

of the calculation, the evaluated probabilities accounted well for the spin-spin effects found in the EPR experiments.

Effect of increasing uptakes of 2,2,6,6-tetramethylpiperidine (DummyT)

The interaction of TEMPO molecules with the zeolite surface sites is favored by the rather high polarity of the radical. For this reason, it is interesting to analyze the effect on the radical-zeolite interaction produced by increasing the loading of a diamagnetic compound that is structurally similar to TEMPO. We selected 2,2,6,6-tetramethylpiperidine, which will be henceforth called "DummyT". Figure 7(a) shows the experimental (full lines) spectra of TEMPO-NaX samples at 0.011 TEMPO molecules per supercage and increasing amounts of DummyT (hydration at about 15 molecules per supercage). The dashed lines in the figure are the spectra computed with the Schneider-Freed program [20]. The results showed that the mobility of the radical decreased with the increase of DummyT concentration up to 0.5-0.6 molecules per supercage. At higher uptakes the mobility remained almost constant. Figure 7(b) reports the variation of the correlation time for motion, obtained by computing the spectra (g and A_N parameters are as used for spectra in Figs 2 and



(a) 3340 3380

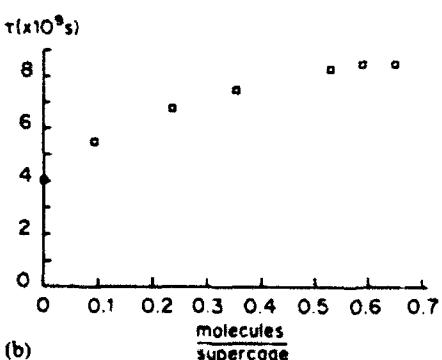


Fig. 7. (a) Experimental (full lines) and computed (dashed lines) EPR spectra of 0.011 TEMPO molecules per supercage adsorbed into NaX zeolite (hydrated at about 15 water molecules per supercage) at different loadings of DummyT (see text), indicated as molecules per supercage. (b) Correlation time for motion as obtained from computation of the spectra as a function of DummyT loading in molecules per supercage.

3), as a function of the DummyT content in the NaX zeolites, expressed in molecules per supercage. The restriction of motion might be interpreted in terms of a preferential occupancy of surface sites: the radical molecules showed a higher selectivity toward surface sites than DummyT. This is expected by considering that DummyT does not carry the polar N-O group (which also may hydrogen bond with the -OH surface groups).

Therefore its interacting ability toward the charged surface sites is lower than for TEMPO radicals. Furthermore, the free volume that the radical molecules occupy may diminish due to filling of the faujasite cavities with DummyT. Nevertheless, our analysis indicated that, at the highest DummyT loading, about 60% of the supercages were occupied. Therefore the TEMPO radicals should retain the same free volume as in the absence of DummyT, but they were forced to occupy more polar surface sites, undergoing restricted mobility. In any case water molecules still occupied the radical environment, since the environmental polarity sensed by the hyperfine coupling did not undergo appreciable variation.

It is interesting to compare the graphs in Fig. 5 and in Fig. 7(b). In both cases the increase in loading leads eventually to a constant value for the spectral parameter indicated in the graph. However the increase in linewidth for TEMPO loading was not so gradual as the increase of correlation time for DummyT loading. Furthermore the constant maximum value of ΔB was reached at lower TEMPO uptake (≈ 0.3 molecules per supercage) compared to the DummyT uptake (≈ 0.5 molecules per supercage) at which a constant maximum value of τ was reached. This different behavior of the two similar substances, TEMPO and DummyT, might be explained on the basis of their different interacting ability toward the zeolite surface sites; the higher polarity of TEMPO molecules favors their preferential localization at surface sites with respect to DummyT molecules.

Effect of pentane addition

All the previous results concern the adsorption of polar molecules which, more or less, compete with the radical for the interaction with the surface. The effect of a non-polar coadsorbate was explored in a qualitative manner by exposing samples of dry NaX zeolite to pentane vapor, which was deposited in a manner similar to that employed for water. To reach saturation from the gas phase,

pentane vapor was passed through the zeolite until no changes in the spectrum were observed. Figure 8 displays the EPR spectra of 0.011 TEMPO molecules per supercage in dehydrated NaX zeolites at different loadings of pentane. In this case too, the spectra were computed (dashed lines) with the aid of the Schneider-Freed program [20]. The two representative spectra, indicated as a and b in Fig. 8, were obtained after 30 and 60 min exposure to a flow of pentane vapor respectively. Spectrum a presented a second adsorption superimposed on signal a, shown in Fig. 1. This second adsorption was characterized by a marked decrease of the A_N tensor components, and of the correlation time for motion if compared with both signal a and signal b. Indeed, the corresponding spectrum in Fig. 8 was computed (dashed line) by using the A_N components 4.5, 6.5 and 35.5 G and $\tau = 8.5 \cdot 10^{-9}$ s. The mobility further increased as saturation was approached (spectrum b in Fig. 8). This spectrum was computed (dashed line) with $\tau = 5.5 \cdot 10^{-9}$ s (a portion of signal a was present, but could not be quantitatively evaluated).

Thus, the effect of pentane was, in our point of view, similar to the effect of water: an increase of

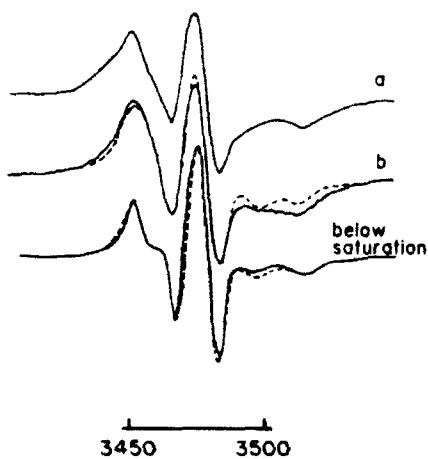


Fig. 8. Experimental (full lines) and computed (dashed lines) EPR spectra of 0.011 TEMPO molecules per supercage adsorbed into dry NaX zeolite, after absorption of pentane. Spectra a and b were recorded after exposure to flowing pentane for 30 and 60 min respectively and indicate the approach to saturation.

mobility with increase of the solvent content. Obviously, in the case of pentane, solvation of the cations could not be a viable mechanism to explain the observation. We therefore concluded that the increase in mobility was due to solvation of the radicals with consequent lack of interaction with the surface. However, after saturation, the resulting EPR spectrum strongly differed from the one obtained by adding water: the mobility again decreased. This effect was ascribed to the characteristics of the pentane solvent: only a few of these large and apolar molecules can enter the zeolite cavity (the maximum allowed amount is 4.2 molecules per supercage [1]) and hardly interact with the charged surface. Under this condition the radicals, as indicated by the A_N tensor components, are no longer exposed to the polar sites at the zeolite surface, but are "squeezed" between pentane molecules which are jammed into a supercage. Therefore, the mobilities of both the radical and the solvent strongly diminish, since the free volume available to the molecules becomes very small.

Conclusions

TEMPO radicals adsorbed into dehydrated X zeolites became localized in two different sites, characterized by different mobility and environmental polarity. These sites were identified as Sites II and III in the faujasite cavities. A rather low activation energy for motion ($< 2.0 \text{ kcal mol}^{-1}$) may be roughly evaluated from the temperature dependence of the correlation time for motion for the two contributions. The addition of both water and pentane increased the mobility of the radicals, due to solvation of the probe molecules, with consequent progressive lessening of the interaction with the surface sites. Nevertheless, 3-4 water molecules per supercage were effective in increasing the radical mobility, which remained almost constant, for radicals adsorbed in the cavities, at water contents larger than 15 molecules per supercage (about three molecules for each Na cation). This indicated that the radicals interacting with the surface allowed only partial hydration and retained

a slow-motion condition ($\tau = 4.0 \cdot 10^{-9} \text{ s}$) even in highly hydrated zeolites.

A decrease of the charge size ratio of the exchanged cation further decreased the mobility of the radicals due to the variation of the local electric field. A decrease of the hydration level at Sites II might be responsible for the observed restriction of mobility in the presence of the larger cations. The same effects were invoked to justify the increased mobility of radicals adsorbed into NaY zeolites with respect to NaX. Increasing amounts of TEMPO radicals were easily adsorbed into the zeolite framework, leading to spin-spin interactions among nearby molecules. Supported by a statistical simulation of the distribution of the TEMPO molecules in the zeolite cavities, it was proposed that two facing N-O groups in the same supercage were responsible for the Heisenberg spin exchange at TEMPO loading > 0.3 molecules per supercage. On the contrary, two radicals in neighboring supercages accounted for the dipolar-dipolar broadening found at loadings up to 0.3 molecules per supercage. Increased loading of 2,2,6,6-tetramethylpiperidine resulted in a restriction of motion of the TEMPO radicals. This was interpreted in terms of preferential occupancy of the charged surface sites by the more polar TEMPO molecules. Also by saturating the zeolite cavities with pentane, the radicals showed a restriction of mobility, but, in this case, the low environmental polarity sensed by the probes indicated pentane solvation of the radicals. Therefore they were trapped in sites rather far from the polar surface. In conclusion both hydrophilic and hydrophobic forces, such as charge and size effects, must be taken into consideration in the case of competition between various molecules for interaction with the X zeolite surface.

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References

- 1 D.W. Breck, *Zeolite Molecular Sieves*, Wiley, New York, 1974.
- 2 J.A. Rabo, *Zeolite Chemistry and Catalysis*, ACS Monograph 171, American Chemical Society, Washington, DC, 1976.
- 3 L. Broussard and D.P. Shoemaker, *J. Am. Chem. Soc.*, 82 (1960) 1041.
- 4 J. Turkevich, *J. Catal. Rev.*, 1 (1968) 1.
- 5 P. Kasai and R.J. Bishop, Jr., in J.A. Rabo (Ed.), *Zeolite Chemistry and Catalysis*, ACS Monograph 171, American Chemical Society, Washington, DC, 1976, p. 350.
- 6 N.N. Tikhomirova and I.V. Nikolaeva, *Zh. Strukt. Khim.*, 10 (1969) 547.
- 7 I.D. Mikheikin, G.M. Zhidomirov and V.B. Kazanskii, *Russ. Chem. Rev. (English Translation)*, 41 (1972) 468.
- 8 C. Naccache and Y. Ben Taarit, *Chem. Phys. Lett.*, 11 (1971) 11.
- 9 N.N. Tikhomirova, I.V. Nikolaeva, V.V. Demkin, E.N. Rosolovskaya and K.V. Topchieva, *J. Catal.*, 29 (1973) 105, 300; 40 (1975) 61.
- 10 G. Martini and L. Burlamacchi, *Chem. Phys. Lett.*, 41 (1976) 129.
- 11 G. Martini, M.F. Ottaviani and G.L. Seravalli, *J. Phys. Chem.*, 79 (1975) 1716.
- 12 L. Kevan and M. Narayana, in G.D. Stucky and F.G. Dwyer (Eds), *Intrazeolite Chemistry*, ACS Symp. Ser. 218, American Chemical Society, Washington, DC, 1982, p. 283.
- 13 G. Martini, M.F. Ottaviani and M. Romanelli, *J. Colloid Interface Sci.*, 115 (1987) 87.
- 14 F. Mazzoleni, M.F. Ottaviani, M. Romanelli and G. Martini, *J. Phys. Chem.*, 92 (1988) 1953.
- 15 M. Romanelli, M.F. Ottaviani, G. Martini and L. Kevan, *J. Phys. Chem.*, 93 (1989) 317.
- 16 G. Martini, M.F. Ottaviani, M. Romanelli and L. Kevan, *Colloids Surfaces*, 41 (1989) 149.
- 17 G. Martini, S. Ristori, M. Romanelli and L. Kevan, *J. Phys. Chem.*, 94 (1990) 7607.
- 18 L.J. Berliner, *Acta Crystallogr. Sect. B*, 26 (1970) 1198.
- 19 J.C.A. Boeyens and G.J. Kruger, *Acta Crystallogr. Sect. B*, 26 (1970) 628.
- 20 J. Schneider and J.H. Freed, in L.J. Berliner and J. Reuben (Eds), *Biological Magnetic Resonance-Spin Labeling Theory and Applications*, Vol. 8, Plenum Press, New York, 1989, p. 1.
- 21 J. Davoust and P.F. Devaux, *J. Magn. Reson.*, 48 (1982) 475. (The computer program was kindly provided by Dr. M.A. Hemminga, Department of Molecular Physics, Wageningen, The Netherlands.)
- 22 J.A.R. Cope, C.L. Gardner, C.A. McDowell and A.I. Pelman, *Mol. Phys.*, 21 (1971) 1043.
- 23 P.E. Pickert, J.A. Rabo, E. Dempsey and V. Schomaker, *Proc. 3rd Int. Congress on Catalysis*, Amsterdam, 1964, p. 714.
- 24 M.M. Dubinin, A.A. Isirkyan, G.U. Rakhmatkariev and V.V. Serpinskii, *Bull. Acad. USSR Chem. Div.*, 4 (1973) 900.
- 25 H. Pfeifer, in P. Diehl, E. Flück and R. Kosfeld (Eds), *NMR: Basic Principles and Progress*, Vol. 7, Springer-Verlag, Berlin, 1972, p. 53.
- 26 H. Lechert and H.W. Henneke, *Surf. Sci.*, 51 (1971) 189.
- 27 H.A. Resing and J.S. Murday, *Adv. Chem. Ser.*, 101 (1973) 314.
- 28 H.A. Resing and J.K. Thomson, *Adv. Chem. Ser.*, 101 (1971) 473.
- 29 E.F. Vansant and J.B. Uytterhoeven, *Adv. Chem. Ser.*, 101 (1971) 426.
- 30 G. Martini, M.F. Ottaviani and M. Romanelli, *J. Colloid Interface Sci.*, 94 (1982) 105.
- 31 M. Romanelli, M.F. Ottaviani and G. Martini, *J. Colloid Interface Sci.*, 96 (1983) 373.
- 32 G. Martini, M. Bindi, M.F. Ottaviani and M. Romanelli, *J. Colloid Interface Sci.*, 108 (1985) 140.
- 33 E. Sackmann and H. Trauble, *J. Am. Chem. Soc.*, 94 (1972) 4492.